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John H. MacMillan's Chemistry Preprint Articles Research and review articles on: Liquid crystals, organometallic compounds, silanes, silicones, platinum catalysts, organophosphines, homogeneous, heterogeneous catalysts, insulating glass sealants, Grignard reagents... Complete list of papers and patents of Dr. MacMillan can be found at: <http://docs.google.com/Doc?docid=0AR2ideyPd9SLZGd3amM5ZmRfMTg3em05Z3Y5Zms&hl=en>

- [Borch_synthesis_of_secondary_aromatic_amines_from_aromatic_nitriles.pdf](#) [164kB] : Borch synthesis of secondary amines from aromatic nitriles
Secondary aromatic amines are readily prepared from aromatic nitriles via a three step sequence involving the intermediacy of a nitrilium salt. A detailed synthesis of a representative secondary amine, 1-[4-(trans-4-Heptylcyclohexyl)phenyl]-N-methylmethanamine, is illustrated. The procedure is applicable for preparing a wide variety of secondary aromatic amines from aromatic nitriles.
- [Aromatic_secondary_amines_from_aromatic_amides.pdf](#) [110kB] : Aromatic secondary amines from aromatic amides
Aromatic secondary amines are produced in nearly quantitative yield by reaction of the corresponding aromatic amide with lithium aluminum hydride in diethyl ether at room temperature. The reaction is applicable to a wide variety of aromatic secondary amines from aromatic amides. A detailed representative synthesis of an aromatic secondary amine is illustrated.
- [Secondary_amides_from_anilines.pdf](#) [103kB] : Secondary amides from anilines
p-Alkyl substituted anilines, such as p-(trans-heptylcyclohexyl)aniline, quickly convert to secondary amides in high yield when treated with acid chlorides in toluene or benzene. The procedure is applicable for preparing a wide variety of secondary amides from aromatic amines. A detailed representative synthetic procedure is presented.
- [Basic_hydrolysis_of_methyl_carbamates_to_amines.pdf](#) [105kB] : Basic hydrolysis of methyl carbamates to amines
Methyl-(p-trans-heptylcyclohexyl)carbamate and other methyl carbamates smoothly hydrolyze and decarboxylate to amines in high yield when refluxed with basic 20% aqueous ethanol. The mixed solvent

system allows solubility of both carbamate and product amine in the reaction medium. A detailed representative synthesis is described.

- [Hoffman degradation of benzamides to carbamates.pdf](#) [155kB] : Hoffman degradation of benzamides to methyl carbamates
4-(trans-4-Propylcyclohexyl)benzamide, 4-(trans-4-Pentylcyclohexyl)benzamide, and 4-(trans-4-Heptylcyclohexyl)benzamide are smoothly converted in high yields to the corresponding methyl carbamates by warming with bromine in dry methanol. The method is applicable to all alkyl or aryl substituted benzamides.
- [Partial hydrolysis of benzonitriles.pdf](#) [146kB] : Partial hydrolysis of benzonitriles to benzamides
4-(trans-4-Propylcyclohexyl)benzonitrile, 4-(trans-4-Pentylcyclohexyl)benzonitrile, and 4-(trans-4-Heptylcyclohexyl)benzonitrile are smoothly hydrolyzed to the corresponding benzamides by refluxing in aqueous potassium hydroxide/ethanol. The method is applicable to all alkyl or aryl substituted benzonitriles.
- [Reduction of a benzonitrile 1- 4- trans-4-Pentylcyclohexyl phenyl methanamine.pdf](#) [113kB] :
Reduction of a benzonitrile; 1-[4-(trans-4-Pentylcyclohexyl)phenyl]methanamine
Alkylcyclohexyl benzonitriles are quantitatively reduced to liquid crystalline amines containing the cyclohexane ring by stirring with lithium aluminum hydride in diethyl ether at room temperature. The procedure is also applicable to *p*-alkyl substituted cyanobiphenyls, which give liquid crystalline biphenylamines. Other benzonitriles should also smoothly reduce to benzylamines. A detailed procedure for a representative reduction is illustrated.
- [Reduced pressure oxidation of propargyl alcohol to aldehyde propynal.pdf](#) [100kB] : Reduced pressure oxidation of propargyl alcohol to aldehyde; Propynal
A detailed modified "Organic Synthesis" procedure for oxidizing propargyl alcohol to the aldehyde propynal is described. The scaled down modified procedure is more practical for laboratory scale.
- [Nitrogen insertion reaction of maleic anhydride-12-5-13.pdf](#) [114kB] : Nitrogen insertion reaction of maleic anhydride; 2-H-1,3-oxazine-2,6(3H)dione
A detailed modified synthesis of "Oxauracil", 2-H-1,3-oxazine-2,6(3H)dione, is described. Higher yields are obtained running this reaction "neat", without solvent.
- [Formation of 1-cyclopenten-1-ylcarbinols from the reaction of excess allylmagnesium chloride with acetylenic alcohols.pdf](#) [410kB] : Formation of 1-cyclopenten-1-ylcarbinols from the reaction of excess allylmagnesium chloride with acetylenic alcohols
1-Cyclopenten-1-yl carbinols were shown to be unexpected byproducts of the reaction of excess allyl magnesium chloride with the internal alkyn carbon of propargyl alcohol or 3-butyne-2-ol, which yield methylene substituted unsaturated alcohols. Propargyl alcohol with allyl magnesium chloride yields, in addition to the expected addition product, 2-methylene-4-pentene-1-ol (1), the cyclic product 1-cyclopenten-1-ylmethanol (2) in 5-10% yields. Likewise, the reaction of excess allyl magnesium chloride with 3-butyne-2-ol yields, in addition to the expected addition product, 3-methylene-5-hexene-2-ol, (3), the cyclic product 1-cyclopenten-1-ylethanol (4) in 5-10% yields.
These compounds are postulated to arise from intra molecular cycloaddition of an intermediate vinyl

carbanion to the terminal vinyl group of the intermediate, followed by hydrolysis. The vinyl carbanion is probably complexed to magnesium ion, which should facilitate additions to the terminal double bond via a cyclic transition state. These reactions are of limited synthetic utility for preparing the cyclopentenyl carbinols. Longer reaction times and larger Grignard/alcohol molar ratios may give more cyclopentenyl products.

- [Mild esterification with diazomethane.pdf](#) [119kB] : Mild esterification with diazomethane
Diazomethane, generated "in situ" from diazald and base, reacts quantitatively with carboxylic acids to yield methyl esters. The method is of greatest utility for unsaturated carboxylic acids with a tendency to isomerize under the strongly acidic esterification methods commonly employed. A detailed preparation for methyl-2E,4E-hexadienoate (sorbate) is described.
- [Chemspider structure depositions.pdf](#) [237kB] : John H. MacMillan's Chemspider organic compounds structure depositions
Listed in chronological order are my complete list of Chemspider structure depositions and data. These compounds are previously unreported or rare materials which were synthesized by me during my career. Combustion data, physical constants, infrared spectra and proton NMR are archived. Download freely any material of interest by clicking the "DATA" link or the other link for the Chemspider structure and reference.
- [Reagent Code Lists for Aiding Students in Determining the Structure of an Organic Chemistry Reaction Product.pdf](#) [2996kB] : Reagent Code Lists for Aiding Beginning Students in Determining the Structure of an Organic Chemistry Reaction Product
Use of reagent code lists allows beginning organic chemistry students to identify the net reactive species, i.e. the "code" for an organic reaction when a set of reagents, solvents and or catalysts are given. For example, the reagent pair dichromate/acid "codes" for oxygen, although not actually present, as the net reactive species. This code allows easier prediction of oxidation reactions with alcohols, alkenes and other groups. The reagent group mercury trifluoro acetate/water/sodium borohydride "codes" for addition of water to an alkene. When presented in tabular format, with reactant, reagent code, active species and product given, the students more easily follow the lecture. The instructor may present the reactions on the board or with slides, then refer the students to the appropriate "reaction codes" on the list. This process allows greater organization of the lecture for both instructor and student, and gives the student an understanding of what is actually occurring in an organic reaction when a series of reagents, solvents and or catalysts is presented for a reaction. Predicting the product becomes much easier and students indicate that they learn the reactions at a faster rate.
- [Mnemonic use for aiding students to determine erythro vs threo stereochemistry in additions to internal alkenes.pdf](#) [407kB] : Mnemonic use for aiding students to determine erythro vs threo stereochemistry in additions to internal alkenes
Use of the TOES mnemonic allows organic chemistry students to quickly write the correct Fischer projections and erythro vs threo nomenclature for additions to the double bonds of internal alkenes.

- [Allyl Grignard addition to the internal alkyne carbon of propargyl alcohol 2-methylene-4-penten-1-ol-Chemspider-published-6-7-13.pdf](#) [421kB] : Allyl Grignard addition to the internal alkyne carbon of propargyl alcohol; 2-methylene-4-penten-1-ol
This compound, previously unreported, was prepared by the room temperature addition of propargyl alcohol to allyl magnesium chloride in ~35% yield. Other Grignards such as methallylmagnesium chloride, propargylmagnesium bromide, and benzylmagnesium chloride added to propargyl alcohol in similar 25-35% yields. The synthesis represents, although in somewhat low yields, a general procedure for 2-methylene-substituted alcohols from inexpensive propargyl alcohol. 5-Hexen-1-yn-3-ol and 3-butyne-2-ol also gave 2-methylene adducts from addition to the internal alkyne carbon.
- [John-Harry-Macmillan-Ph.D.-Thesis-Organic-Chemistry-Northeastern-University-1970-Retyped.pdf](#) [7742kB] : John Harry MacMillan Ph.D. Doctoral Dissertation Organic Chemistry Northeastern University 1970, Retyped
This thesis is here retyped with modern fonts from the original scanned document.
Triple Bond Participation in the Oxy-Cope Rearrangement, Northeastern University, Doctoral Dissertation, Organic Chemistry, 1970.
As a part of the study of oxy-Cope systems in this laboratory, some examples of triple bond participation in these reactions have been investigated. In general, the experimental results indicate that acetylenes and allenes participate readily in cyclic six membered transition states and that triple bond participation in electrocyclic reactions leads to increased rates in comparison with the corresponding olefinic structures. 1-Hexen-5-yn-3-ol was subjected to vapor phase thermolysis in a flow system over the range of 350-90 degrees centigrade and under various pressures. The extent of beta-hydroxyolefin cleavage, which leads to formation of acrolein and allene, is independent of residence time in the thermolysis zone but increases with temperature, indicative of a higher activation energy than for the competing rearrangement processes. One of these processes affords 4,5-hexadienal via an acetylenic analog of the oxy-Cope reaction. Also produced is 3-cyclopentenecarboxaldehyde in amounts increasing with increasing temperature and/or residence time. The data is consistent with an electrocyclic reaction involving the enolic progenitor of the oxy-Cope product, which ketonizes only upon condensation in the product trap. The thermolysis of 3-methyl-1-hexen-5-yn-3-ol was reinvestigated due to conflicting literature reports concerning product formation. The production of both vinyl acetylcyclopropane and 4-acetylcyclopentene has been verified in this laboratory. The effect of the methyl group upon product composition is interpreted on the basis of a torsional effect in the transition state. Thermolysis of 5-hexen-1-yn-3-ol affords 2- and 3- cyclopentenecarboxaldehydes, trans-2,5-hexadienal and sorbaldehyde in varying amounts dependent upon temperature and contact time. Since the competing beta-hydroxyolefin cleavage is completely absent, kinetic parameters could be determined. The Arrhenius energy of 30 kcal/mol and activation entropy of -14 e.u. are indicative of a concerted mechanism. The kinetic data, the effects of temperature and contact time upon product distribution and the results of a deuterium tracer study indicate the intermediacy of the primary oxy-Cope product in the formation of all observed products. These reactions constitute the chemistry of an allenol intermediate, 1-hydroxy-1,2,5-hexatriene.

Thermolysis of 1-phenyl-3-butyn-1-ol and 1-phenyl-2-methyl-3-butyn-2-ol gave no trace of oxy-Cope rearrangement products, indicating the unwillingness of the phenyl group to participate in the oxy-Cope rearrangement. Thermolysis of 1,5-hexadiyn-3-ol at 350 degrees gives 4-methylene-2-cyclobutene-1-carboxaldehyde and phenol. The hydroxy group greatly facilitates the aromatization pathway. Phenol production increases with increasing temperature or residence time. 3-Methyl or 4,4-dimethyl substitution blocks the pathway leading to aromatization. 4-Methyl substitution gives o-cresol as the only aromatic product. The data indicate the absence of hydroxy migration or carbon skeletal rearrangements in the formation of phenol. Prismane or benzvalene intermediacy is ruled out on the basis of this data. A mechanism for phenol formation is presented involving the intermediacy of the primary oxy-Cope product. Thermolysis of 5-hexyn-3-ol and 2-methyl-4-pentyn-2-ol afford quantitative conversions to cleavage products. Kinetic studies show both reactions to be first order and to possess highly negative entropies of activation, indicative of concerted mechanisms with cyclic transition states. Both alcohols gave faster cleavage rates and lower activation energies than the corresponding literature values of their olefinic analogs. Grignard reagents are found to add to the internal carbon atom of the triple bond in propargylic alcohols to yield 2-methylene substituted alcohols. The presence of a carbinol function bonded to the internal alkyne carbon atom is necessary for the addition to occur. Dissert. Abstr. Int. B, Vol. XXXII, No. 10, 1972 Order No. 72-13

- [Addition of Allyl Magnesium Chloride to Propynal-published-12-20-12.pdf](#) [58kB] : Addition of Allyl Magnesium Chloride to Propynal ; 5-Hexen-1-yn-3-ol
Allyl magnesium chloride adds to propynal (propargyl aldehyde) in good yields, giving 5-hexen-1-yn-3-ol after decomposition of the Grignard complex over ice/ammonium chloride. Propynal is readily prepared in reproducible yields by the Organic Synthesis procedure. This reaction can be readily applied to other alkynes and Grignard reagents to generate a variety of acetylenic alcohols.
- [The Acetylenic-Oxy-Cope Rearrangement of 1,5-Hexadiyne-3-ol and Methyl Substituted Derivatives.pdf](#) [3577kB] : The Acetylenic-Oxy-Cope Rearrangement of 1,5-Hexadiyne-3-ol and Methyl Substituted Derivatives
Vapor phase thermolysis of 1,5-hexadiyne-3-ol at 350°C afforded phenol and 4-methylene-2-cyclobuten-1-carboxaldehyde as products. The 4-methyl derivative gave only ortho cresol and 4-ethylidene-2-cyclobutene-1-carboxaldehyde. The 3-methyl and 4,4-dimethyl derivatives yielded no aromatic products. 3-Acetyl-4-methylene cyclobutene was the sole product from thermolysis of the 3-methyl derivative, while 4-isopropylidene-2-cyclobutene-1-carboxaldehyde was the sole product from thermolysis of the 4,4-dimethyl derivative. The phenol and ortho-cresol aromatic products are postulated to result from cyclization of intermediate 1-hydroxy-1,2,4,5-tetraenes (bis allenes), produced by acetylenic oxy-Cope rearrangements. Subsequent supra facial 1,5-hydrogen shifts restore the aromaticity. The 3-methyl and 4,4-dimethyl derivatives cannot aromatize by this pathway. Exclusive formation of ortho cresol eliminates prismane or benzvalene intermediates, as such structures should also produce meta and para cresols. The mechanism of cyclobutene derivative formation for all compounds is proposed to involve cyclization

of the identical bis allenes, via diradical pathways. The 3-hydroxy functionality greatly facilitated the rate of the aromatizations, consistent with rate accelerations seen in other oxy-Cope and acetylenic oxy-Cope systems.

- [Addition_of_propargyl_allyl_and_benzyl_Grignard_reagents_to_alpha_beta_unsaturated_alcohols.pdf](#) [4889kB] : Addition of propargyl, allyl and benzyl Grignard reagents to α , β -unsaturated alcohols
 α , β -Unsaturated alkenyl or propargyl alcohols add propargyl, allyl and benzyl Grignard Reagent at the β -position of the alcohol, yielding methylene or methyl substituted alcohols in moderate yield. Alkenes and alkynes with no alcohol functionality or alcohols with no α , β -unsaturated functionality failed to react. Saturated Grignards gave very low yields. The mechanism is postulated to involve a cyclic transition state with an initial complex of the hydroxyl on the alcohol to the magnesium of the Grignard. The reaction has synthetic utility for the production of 2-methylene substituted alcohols.
- [Addition_of_propargyl_Grignard_to_aldehyde_1-Phenyl-3-butyne-1-ol.pdf](#) [580kB] : Addition of propargyl Grignard to aldehyde; 1-Phenyl-3-butyne-1-ol
 In order to avoid an internal rearrangement of the propargyl Grignard reagent, a modification of the procedure reported by Sondheimer was utilized. The procedure involved low temperature preparation of the Grignard reagent, catalyzed by mercuric chloride. For example, without this modification, a room temperature standard Grignard synthesis of 1-hexen-5-yne-3-ol gave an approximate 50/50 mixture of desired product and the rearranged internal alkyne product 1-hexen-4-yn-3-ol. This reaction gives reproducible yields in the 60-80% range. No trace of product alcohols resulting from rearrangement of propargyl Grignard to internal acetylenic or allenic species could be detected under these conditions.
- [Acetylenic_Alcohols.pdf](#) [940kB] : Preparation of acetylenic alcohols by addition of propargyl Grignard reagents activated at low temperatures with mercury ion to α , β -unsaturated aldehydes and ketones.
 Addition of propargyl Grignard reagents to α , β -unsaturated aldehydes and ketones, with Grignards synthesized at low (-30 to -10 °C) temperatures and activated at these temperatures by trace amounts of mercuric chloride, gave acetylenic alcohols in good yields. No trace of products resulting from rearrangement of propargyl Grignards to internal acetylenic or allenic species could be detected. In contrast, room temperature reactions gave alcohol product mixtures resulting from the rearrangement of propargyl Grignards to internal alkynyl or allenyl Grignards. This synthetic modification is of great utility in preparation of alcohol precursors for annulene synthesis or acetylenic oxy Cope rearrangements.
- [Facile_N-methylation_of_amide_functional_heterocycles_with_dimethyl_sulfate.pdf](#) [893kB] : Facile N-Methylation Reaction of Amide Functional Heterocycles with Dimethyl Sulfate.
 4 and 5-substituted 1,3(3H) oxazine-2,6-diones (oxauracils) are easily alkylated under mild conditions with dimethyl or diethyl sulfate in boiling acetone and slurry of sodium bicarbonate. Workups are straight forward and yields typically in the 60-70% range. The reaction should prove of utility also for alkylating uracils and other amide functional heterocycles.
- [Chiral-Liquid-Crystalline-Nitrones.pdf](#) [6124kB] : Preparation, mesogenic behavior and photochemistry of homologous chiral liquid crystalline nitrones.
 A series of chiral N-(p-2-methoxybutoxyphenyl)- α -(p-n-alkoxyphenyl) nitrones, was prepared and

examined for mesogenic properties. The methyl derivative showed only a transient cholesteric texture on rapid supercooling, while the ethyl homolog was a monotropic cholesteric. The propyl and butyl homologs were non mesogenic while the pentyl derivative showed a monotropic chiral Sc mesophase. The higher members of the series were enantiotropic, exhibiting only chiral Sc mesophases. The materials exhibited both thermal and photochemical instability, however, suitable eutectization resulted in lower temperature chiral Sc and cholesteric phases with adequate stability under long wavelength (> 400 nm) illumination.

- [Aryl maleic Anhydrides.pdf](#) [2501kB] : Detailed synthetic procedures for aryl maleic anhydrides; p-bromophenyl maleic anhydride and other aryl substituted maleic anhydrides. Detailed synthetic procedures and spectral data for the synthesis of aryl substituted maleic anhydrides are listed.
- [Synthesis of unreported 4- and 5-Aryl Substituted 1,3,3H Oxazine-2,6-Diones.pdf](#) [2264kB] : Detailed Synthetic Procedure for 4-(4-bromophenyl)-1,3(3H) Oxazine-2,6-Dione and related 4 and 5-aryl substituted -1,3(3H) Oxazine-2,6-Diones. Spectroscopic and analytical data are included.
- [Reaction-of-acrylonitrile-with-trimethylsilyl-azide.pdf](#) [922kB] : The Reaction of Acrylonitrile with Trimethylsilyl Azide
Acrylonitrile (1) on reaction with trimethylsilyl azide (2) gave complex mixtures, with 3-imino-2-trimethylsilyl propionitrile (4) being the major isolatable product in low yield. The reaction was slow even in high boiling solvents due to the electron withdrawing cyano group decreasing the nucleophilicity of the conjugated double bond. Considerable intractable polymer was always produced. The mechanism is believed to involve anti-Markonikov 1,2 addition of trimethylsilyl azide (2) to the double bond of 1, giving intermediate 3-azido-2-trimethylsilyl propionitrile (3). Loss of nitrogen gives imine (4). The mechanism is supported by the detection of an intermediate believed to be 3 on g.c. analysis, which rapidly disappeared giving 4. The reaction is of limited synthetic utility due to the slow rate and tendency of acrylonitrile to polymerize even with inert solvent added as diluent.
- [reaction_napthoquinones_with_trimethylsilyl_azide.pdf](#) [271kB] : Further Studies of the Interaction of Carbonyl Compounds with Organometallic Azides, the Reaction of Napthoquinones with Trimethylsilyl Azide.
1,4-Napthoquinone and 1,2 Napthoquinone on reaction with trimethylsilyl azide gave complex mixtures, with 2-amino-1,4-napthoquinone and 4-amino-1,2-napthoquinone being the major isolatable products. The mechanism is believed to involve conjugate 1,4 addition of trimethylsilyl azide to an α,β -unsaturated carbonyl carbon, giving intermediate trimethylsiloxy azide adducts. Loss of nitrogen gives imine intermediates, which on hydrolysis and tautomerization give amino napthoquinones. The mechanism is supported by the isolation of an adduct of the proposed intermediate with 1,4-napthoquinone. Anthraquinone fails to react, also consistent with this mechanism, as 1,4 addition of trimethylsilyl azide would disrupt the aromaticity of one ring.
- [aryl-oxauracils.pdf](#) [46kB] : Synthesis of Additional 4 and 5-Aryl Substituted 1,3(3H) Oxazine-2,6-Diones. Additional 4-and 5-Aryl Substituted 1,3(3H) oxazine-2,6-diones (oxauracils) were synthesized for anti malarial screening by the reaction of the corresponding aryl maleic anhydride with trimethylsilyl azide, by

the procedure described in J. Heterocyclic Chemistry, Vol. 12, p 1215, (1975). The N-Alkylated derivatives were prepared by refluxing the corresponding aryl substituted oxauracil with a di alkyl sulfate/sodium bicarbonate slurry in acetone, as described in the above paper.

- [EuFOD-Shift-Data.pdf](#) [5850kB] : Supplemental Unpublished Original Notebook Chemical Shift Data Supporting J.H. MacMillan and S.S. Washburne,
This material is additional supplemental original notebook chemical shift data supporting J.H. MacMillan and S.S. Washburne, "Lanthanide Chemical Shift Reagents as Tools for Determining Isomer Distributions in 2,4-Hexadieneoates and Related Compounds", Organic Magnetic Resonance, Vol.6, p250,(1974). This research was performed at Temple University in 1973,sponsored under Grant No. CA-1 3120-02 from the National Cancer Institute. The original notebook entries were scanned for this document. They are handwritten but nearly all legible.
- [phenyl.pdf](#) [1215kB] : Investigation of Possible Phenyl Participation in the Oxy-Cope and Acetylenic Oxy-Cope Rearrangements.
Vapor Phase thermolysis of 1-phenyl-3-butyne-1-ol and 1-phenyl-2-methyl-3-butyne-2-ol in the gas phase or liquid phase failed to yield the expected oxy-Cope products, even at elevated temperatures and with protracted reaction times. 1-Phenyl-3-butyne-1-ol cleaved to benzaldehyde and allene, while 1-phenyl-2-methyl-3-butyne-2-ol was completely unreactive. The data indicate that the disruption of the aromatic ring necessary for the Oxy-Cope reaction to occur results in too high an activation energy. Claisen Rearrangements, by contrast, proceed readily under these conditions. The activating effect of the ether oxygen atom in Claisen rearrangements may lower their activation energy compared to oxy-Cope systems.
- [virtual-laboratory.pdf](#) [115kB] : Virtual Chemistry Laboratory for Non-Science Majors, Good, Bad or Both?
The author's experiences with a totally virtual chemistry laboratory versus the traditional hands on laboratory are summarized and analyzed, together with the advantages and disadvantages of both approaches. A compromise program is favored, where computerized instruction is integrated with the classical program, both to minimize lab costs for the school or University, and to provide real world lab experience for the students.
- [constructivist.pdf](#) [155kB] : Constructivist (hands on) theories for high school chemistry curricula are reviewed and critiqued. The authors own experiences with this learning technique are described. Advantages and disadvantages of constructivist learning versus traditional chemistry education are discussed.
- [Tufts-Thesis.pdf](#) [7265kB] : John H. MacMillan, Undergraduate Thesis, Tufts University, 1966
Subjects: Vanadium Hydride, Palladium Hydride, Vanadium Hydride X-ray line broadening, Magnetic Susceptibility of Palladium Hydride, Non Stoichiometric Hydrides.
- [The_Magnetic_Susceptibility_of_Palladium_Hydride_J._Phys._Chem._Vol._70_p3024_1966.pdf](#) [114kB] : MacMillan Publication 1
- [Vapor_Phase_Thermolysis_of_1-Hexen-5-yn-3-ol_An_Acetylenic_Oxy-Cope_Reaction_J._Amer._Chem._Soc._Vol._90_p_6141_1968.pdf](#) [700kB] : MacMillan Publication 2

- [A Novel Steric Effect in the Thermolysis of Prop-2-ynyl Vinyl Carbinols Chemical Communications p 301 1970.pdf](#) [200kB] : MacMillan Publication 3
- [The Vapor Phase Acetylenic Oxy-Cope Reaction of 5-Hexen-1-yn-3-ol The Chemistry of an Allenol Intermediate J. Amer. Chem. Soc. Vol. 92 p 2404 1970.pdf](#) [1079kB] : MacMillan Publication 4
- [Participation of Acetylenic Bonds in Pericyclic Reactions Thermal Cleavage of Beta-Hydroxyacetylenes J. Amer. Chem. Soc. Vol. 93 p 6967 1971.pdf](#) [1352kB] : MacMillan Publication 5
- [Reaction Rates by Flow System Thermolysis The Competitive Components of the Oxy-Cope Reaction Chemical Communications p 936 1971.pdf](#) [232kB] : MacMillan Publication 6
- [Interaction of Carbonyl Compounds with Organometallic Azides Part V. Sorboyl Chloride and its Conversion to an Alpha-Pyridone J. Org. Chem. Vol. 38 p 2982 1973.pdf](#) [443kB] : MacMillan Publication 7
- [Lanthanide Chemical Shift Reagents as Tools for Determining Isomer Distributions in 2,4-Hexadiene-2-ones and Related Compounds Organic Magnetic Resonance Vol. 6. p250 1974.pdf](#) [294kB] : MacMillan Publication 8
- [Recent Examples of Selectivity in Catalysis Strem Chemiker Vol. 11 No. 2 July 1974.pdf](#) [1307kB] : MacMillan Publication 9
- [Synthesis of Substituted 2H-1,3-Oxazine-2,6-Diones by Reaction of Trimethylsilyl Azide with Maleic Anhydrides J.Org.Chem. Vol. 40 p 743 1975.pdf](#) [556kB] : MacMillan Publication 10
- [Further Investigation of the Interaction of Trimethylsilyl Azide with Substituted Maleic Anhydrides Synthesis of 4- and 5-Aryl Substituted 1,3,3H-Oxazine-2,6-Diones J.Heterocyclic Chemistry Vol. 12 p 1215 1975.pdf](#) [677kB] : Publication Number 11
- [Improved Procedure for the Preparation of Oxauracil 2H-1,3,3H-Oxazine-2,6-Dione Organic Preparations and Procedures Int. Vol. 9. p 87 1977.pdf](#) [198kB] : Publication Number 12
- [Low Transition Temperature Liquid Crystalline Amines Incorporating the Trans-1,4-Cyclohexane Ring System Molecular Crystals and Liquid Crystals Vol. 55 p 61 1979.pdf](#) [804kB] : Publication Number 13
- [Induced Phases in Terminal Mixtures of Polar Liquid Crystalline Amines and Nitriles Mol. Crystals and Liquid Crystals Letters Vol. 56 p7 1979.pdf](#) [322kB] : Publication Number 14
- [Low Transition Temperature Liquid Crystalline Amines Incorporating the Biphenyl Ring System Mol. Crystals and Liquid Crystals Letters Vol. 56 p51 1979.pdf](#) [394kB] : Publication Number 15
- [Amine Substituted Liquid Crystal Compositions U.S. Patent 4,293,193 Oct. 6 1981.pdf](#) [335kB] : MacMillan U.S. Patent Number 1

- [One Package Heat Curable Sealant Compositions U.S. Patent 4 430 489 Feb. 7 1984.pdf](#) [762kB] : MacMillan U.S. Patent Number 2
- [Thioether Modified Polymer Compositions U.S. Patent 4 590 240 May 20 1986.pdf](#) [530kB] : MacMillan U.S. Patent Number 3
- [Method for the preparation of aminopropyl or aminoalkyl functional polyalkyl or aryl siloxanes . United States Patent 6 177 583 January 23 2001.pdf](#) [347kB] : MacMillan U.S. Patent Number 4
- [Siloxane modified carboxylic acid substituted amines and salts thereof U.S. Patent 6 489 499 December 3 2002.pdf](#) [479kB] : MacMillan U.S. Patent Number 5
- [Supported aldehydic silanes and method of manufacture U.S. Patent 6 589 799 July 8 2003.pdf](#) [446kB] : MacMillan U.S. Patent Number 6
- [Supported aldehydic silanes and method of manufacture U.S. Patent 7 045 365 May 16 2006.pdf](#) [545kB] : MacMillan U.S. Patent Number 7
- [One Package Heat Curable Sealant Compositions U.S. Patent 4 430 489 Feb. 7 1984.pdf](#) [762kB] : MacMillan U.S. Patent Number 12
- [Japanese-Strem-Chemiker-1974.pdf](#) [5654kB] : Japanese Edition of "Recent Examples of Selectivity in Catalysis", by John H. MacMillan, Strem Chemicals, July, 1974.
- [Vanadiun-Line-Broadening.pdf](#) [3003kB] : **T.R.P. Gibb Jr.** and **John H. MacMillan**, Vanadium hydride x-ray line broadening
The broadening of the x-ray diffraction lines of non stoichiometric vanadium hydrides of composition VH_{0.15} to VH_{0.80} were measured and compared to pure vanadium powder. The 110,200,211,220,310 and 321 diffraction planes line broadening were measured at all stoichiometries. In every case the 211 plane showed the greatest percentage broadening, followed by the 200 plane. The broadening order was 211>200>110=310>321.
The results were interpreted to possibly indicate preferential distortion of the 211 plane due to its smallest unit cell area and greatest percentage lattice deformation on hydrogen occupancy of octahedral sites.
- [bioconext.pdf](#) [42kB] : A method for derivatizing surfaces with aldehyde groups by employing a new alkoxy aldehydic silane. **Coyne, Ann. N., Benner, Lauren., MacMillan, John H., Telepchak, Michael T.** *A new line of trialkoxy aldehydic silanes, manufactured by United Chemical Technologies, Inc. under the trademark BIO-CONEXT, allows the one-step addition of an activated surface directly to a matrix, thus circumventing the steps and reagents required by other methods. In addition, the covalent linkage formed by this method has only one Schiff base, yielding a much more stable product. Furthermore, this method can be used with any matrix that has either naturally occurring or synthetically incorporated hydroxyl groups that can be synthetically modified with trialkoxy aldehydic silanes. Included are some of the most popular and useful matrix materials, such as glass, agarose, silica, glass-coated ELISA plates, metals such as nickel and paramagnetic iron, and some commercially available resins¹. In addition, incorporation of trialkoxy aldehydic silanes with different chain lengths can be used to prevent crowding of large bio-molecules and to allow access to active sites. In this report, we describe and evaluate the BIO-CONEXT method for covalent attachment of bio-molecules.*

- [Nitrones-2.pdf](#) [3076kB] : Synthesis and Photochemistry of Chiral Liquid Crystalline Nitrones
 - [Grignard-addition-to-propargylic-allylic-alcohols.pdf](#) [1467kB] : Addition of Grignard Reagents to Allylic and Propargylic Alcohols
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- [acetylenes.pdf](#) [944kB] : Vapor Phase Thermolysis of 1,5-Hexadiynes, Effect of Hydroxyl Substitution
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- [diphenylacetylene2.pdf](#) [401kB] : An Improved Method for the Preparation of Bis-DiphenylPhosphino Acetylene and unsymmetrical Aryl Substituted Diphenylphosphino Acetylenes
 - [polyformals-2.pdf](#) [3415kB] : Hexamethylene Glycol Polyformal Copolymers for Insulating Glass and Building Sealants
 - [ArylMaleic-Anhydrides.pdf](#) [2185kB] : A Facile General Synthesis of ArylMaleic Anhydrides:
By a sequence involving Knoevenagel condensation, Michael addition of cyanide, hydrolysis, and selenium dioxide oxidation, a series of seven aryl maleic anhydrides were prepared in excellent overall yields. The regiospecificity of reaction of these anhydrides with various nucleophilic species, e.g. Me3SiN3, NH3, and PhNH2 was investigated. Except for a few cases, the nucleophile attacks the more hindered carbonyl, in a reaction controlled by electronic rather than steric factors. These anhydrides are of particular utility in the synthesis of 4-and 5-Aryl Substituted 1,3(3H) Oxazine-2,6-Diones (Oxauracils).
 - [Oxauracils-Hydrolysis.pdf](#) [4903kB] : Hydrolysis reactions of the 4-and 5-Alkyl or Aryl Substituted 1,3(3H) Oxazine-2,6-Diones (Oxauracil) Ring System
Acid or base hydrolysis of 4-Aryl or alkyl Substituted 1,3(3H) Oxazine-2,6-Diones (Oxauracils) 1,2 yield alkyl or aryl methyl ketones, 6, and ammonia. An intermediate beta keto acid, 5, could be isolated under mild conditions. N-alkylated oxauracils give the same methyl ketones and alkylamines. The N-alkylated oxauracils hydrolyze faster than the non alkylated oxauracils in competition experiments, probably due to electronic factors. 5-aryl oxauracils hydrolyze slower than the 4-isomers in direct competition experiments, probably due to steric factors at the C-6 carbonyl carbon. A mechanistic scheme is presented involving nucleophilic attack at the C-6 carbonyl, decarboxylation of the resulting amino acid 2 yielding enamine 3, which tautomerizes to imine 4. Hydrolysis of 4 and further decarboxylation of beta keto acid 5 give methyl ketones 6 in nearly quantitative yield. The in vitro toxicity of these products is low, thus is of little concern in genetic studies involving substitution of oxauracils for uracils in RNA or other nucleotides.

- [surface.pdf](#) [38kB] : Silane Surface Modifying Reagents

Industrial silane suppliers offer a wide range of polar and non-polar silanes which may be used to modify the surface of substrates such as glass, silica, alumina, silicon and transition metals. The surface may be treated to decrease wettability or increase adhesion of the polymer to glass, silicon or metals. Such treatment may also allow differential polar or hydrophobic interactions. The hydrophobic class represents alkyl functional alkoxy or chlorosilanes from C2-C22 chain length. They find use in decreasing the wettability of treated surfaces, as releasing agents and for increasing the hydrophobic interactions of treated sorbents with diluents in a mobile phase.

- [MacMillan_PhD_Thesis.pdf](#) [13016kB] : Triple Bond Participation in the Oxy-Cope Rearrangement ,Ph.D. Thesis, John H. MacMillan, original scanned document.

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